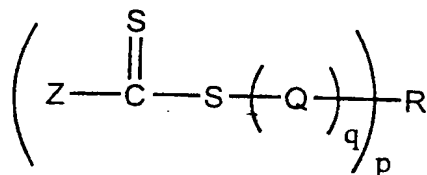


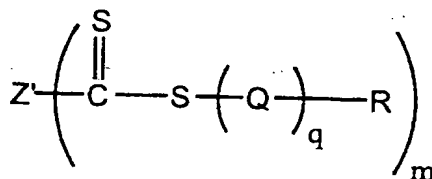
WHAT IS CLAIMED IS:

1. A process for the synthesis of polymers selected from the group consisting of:



Formula A

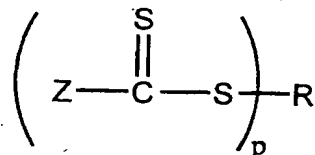
and



Formula B

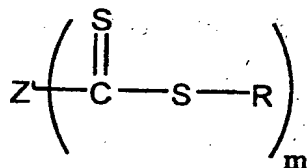
comprising contacting:

- 10 (i) a monomer having repeating units, Q, selected from the group consisting of vinyl monomers of structure  $\text{CH}_2=\text{CUV}$ , maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;
- (ii) a thiocarbonylthio compound selected from:



Formula C

and



Formula D

having a chain transfer constant greater than about 0.1; and

- 20 (iii) free radicals produced from a free radical source; and controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

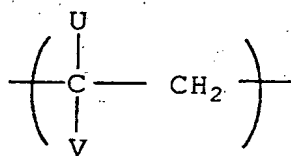
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the polymer of Formula B being made by contacting (i), (ii) D and (iii);

5 wherein:

Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy-carbonyl, optionally substituted aryloxy-carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O<sub>2</sub>CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato [-P(=O)R"2], and a polymer chain formed by any mechanism;

15 Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



20

and

repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

25 U is selected from the group consisting of hydrogen, halogen, optionally substituted C<sub>1</sub>-C<sub>4</sub> alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aryloxy (O<sub>2</sub>CR"), alkoxy-carbonyl and aryloxy-carbonyl (CO<sub>2</sub>R");

30 V is selected from the group consisting of hydrogen, R", CO<sub>2</sub>H, CO<sub>2</sub>R", COR", CN, CONH<sub>2</sub>, CONHR", CONR"2, O<sub>2</sub>CR", OR" and halogen;

R is selected from . group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; in compounds C and D, R• is a free-radical leaving group that initiates free radical polymerization;

R" is selected from the group consisting of optionally substituted C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>2</sub>-C<sub>18</sub> alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when  $p \geq 2$  then  $R=R'$ ;

m is an integer  $\geq 2$ ; and

R' is a p-valent moiety selected from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; in compounds C and D, R'• is a free radical leaving group that initiates free radical polymerization.

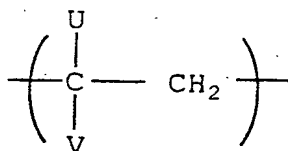
2. A process according to Claim 1 comprising controlling polydispersity by varying the ratio of the number of molecules of (ii) to (iii) as follows:

- 5 (a) lower polydispersity by increasing the ratio of (ii) to (iii); and  
 (b) increase polydispersity by decreasing the ratio of (ii) to (iii).

3. A process according to Claim 2 comprising increasing the ratio of (ii) to (iii) and obtaining a polymer having a polydispersity below about 1.5.

10

4. A process according to Claim 1 comprising selecting the following monomer repeating unit:

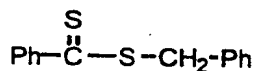


from (i).

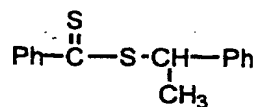
15

5. A process according to Claim 1 comprising selecting the monomer units Q and the value of q so that when  $q \geq 1$  and Q is a single monomer species, then the polymer is homopolymer; when  $q \geq 2$  and Q is selected from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and when  
 20  $q \geq 2$  and Q is selected from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then the polymer is block copolymer.

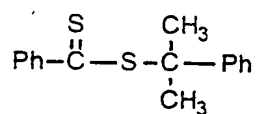
6. A process according to Claim 1 wherein the thiocarbonylthio compound is  
 25 selected from the group consisting of:



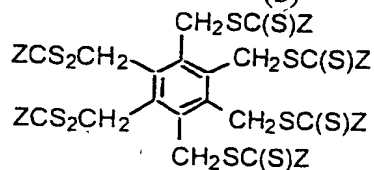
(3)



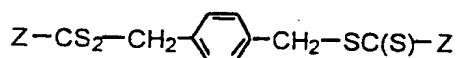
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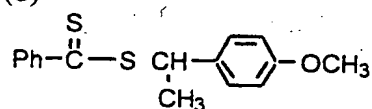
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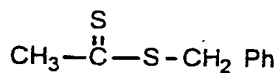
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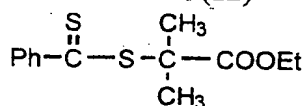
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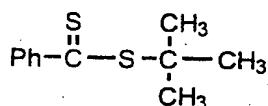
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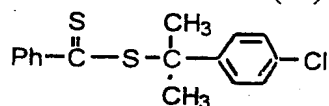
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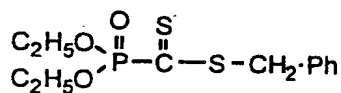
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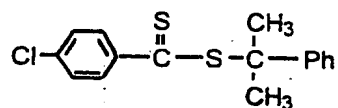
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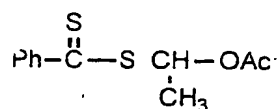
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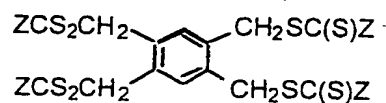
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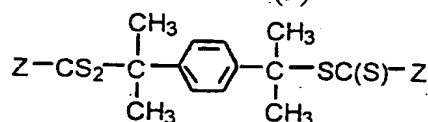
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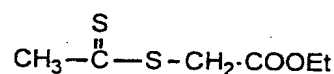
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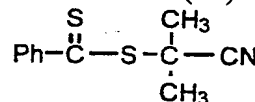
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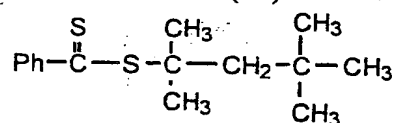
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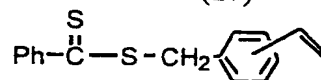
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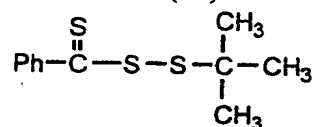
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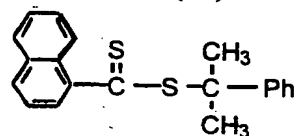
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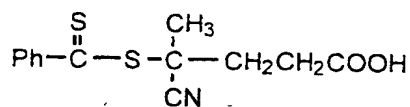
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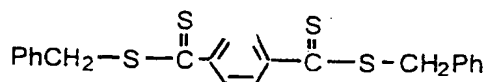
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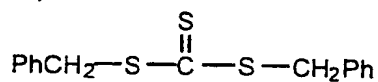
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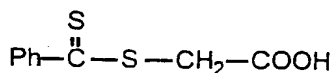
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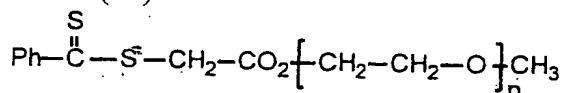
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(26)

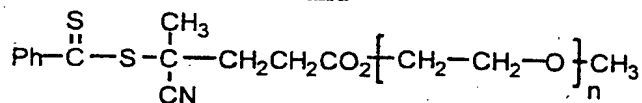


(27)



(28)

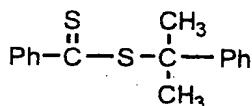
and



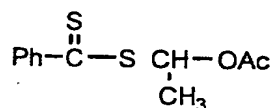
(29)

10 wherein Z is phenyl.

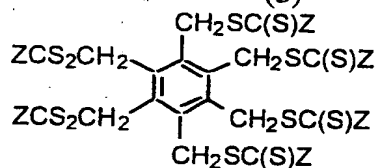
7. A chain transfer agent selected from the group consisting of:



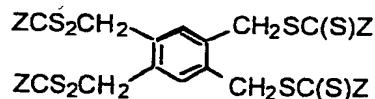
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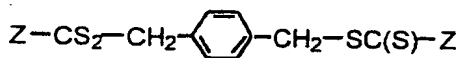
(6)



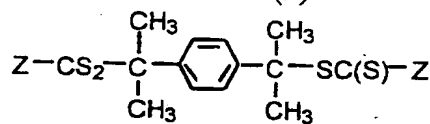
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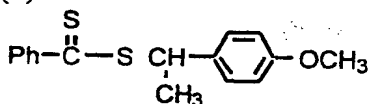
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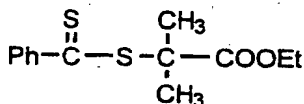
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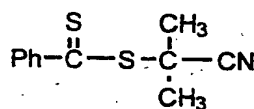
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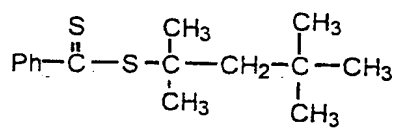
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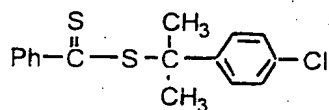
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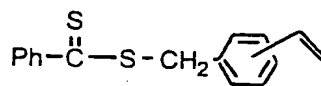
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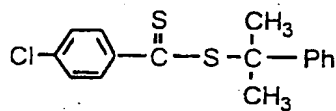
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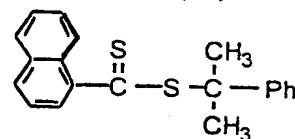
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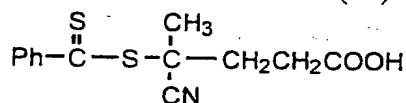
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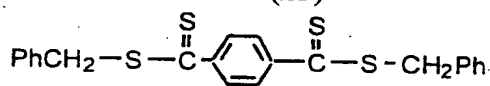
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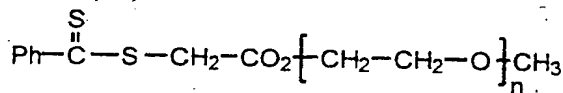
(23)



(24)

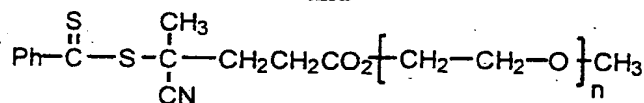


(25)



(28)

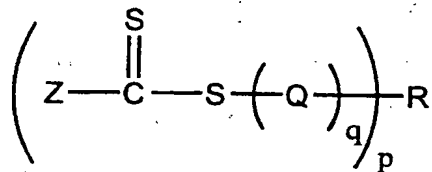
and



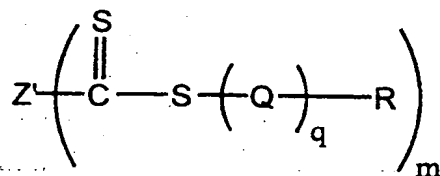
(29)

wherein Z is phenyl.

8. A polymer of the Formula



Formula A



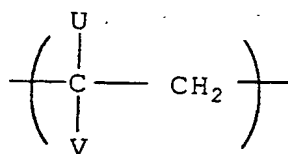
Formula B

wherein:

Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy-carbonyl or  
 5 optionally substituted aryloxy-carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O<sub>2</sub>CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato [-P(=O)R"2], and a polymer chain formed by any mechanism;

10 Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

15 Q is selected from the group consisting of



and

repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

20 U is selected from the group consisting of hydrogen, halogen, optionally substituted C<sub>1</sub>-C<sub>4</sub> alkyl, wherein the substituents are independently selected from the group consisting of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aroyloxy (O<sub>2</sub>CR"), alkoxy-carbonyl and aryloxy-carbonyl (CO<sub>2</sub>R");

25 V is selected from the group consisting of hydrogen, R", CO<sub>2</sub>H, CO<sub>2</sub>R", COR", CN, CONH<sub>2</sub>, CONHR", CONR"2, O<sub>2</sub>CR", OR" and halogen;

R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or  
 30 heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; R• being derived from a free radical leaving group that initiates free radical polymerization;



R<sup>'''</sup> is selected from the group consisting of optionally substituted C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>2</sub>-C<sub>18</sub> alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when p ≥ 2, then R = R';

m is an integer ≥ 2; and

R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; R'• being derived from a free radical leaving group that initiates free radical polymerization.

9. A polymer according to Claim 8 selected from the group consisting of random, block, graft, star and gradient copolymer.

10. A polymer according to Claim 9 having end group functionality.